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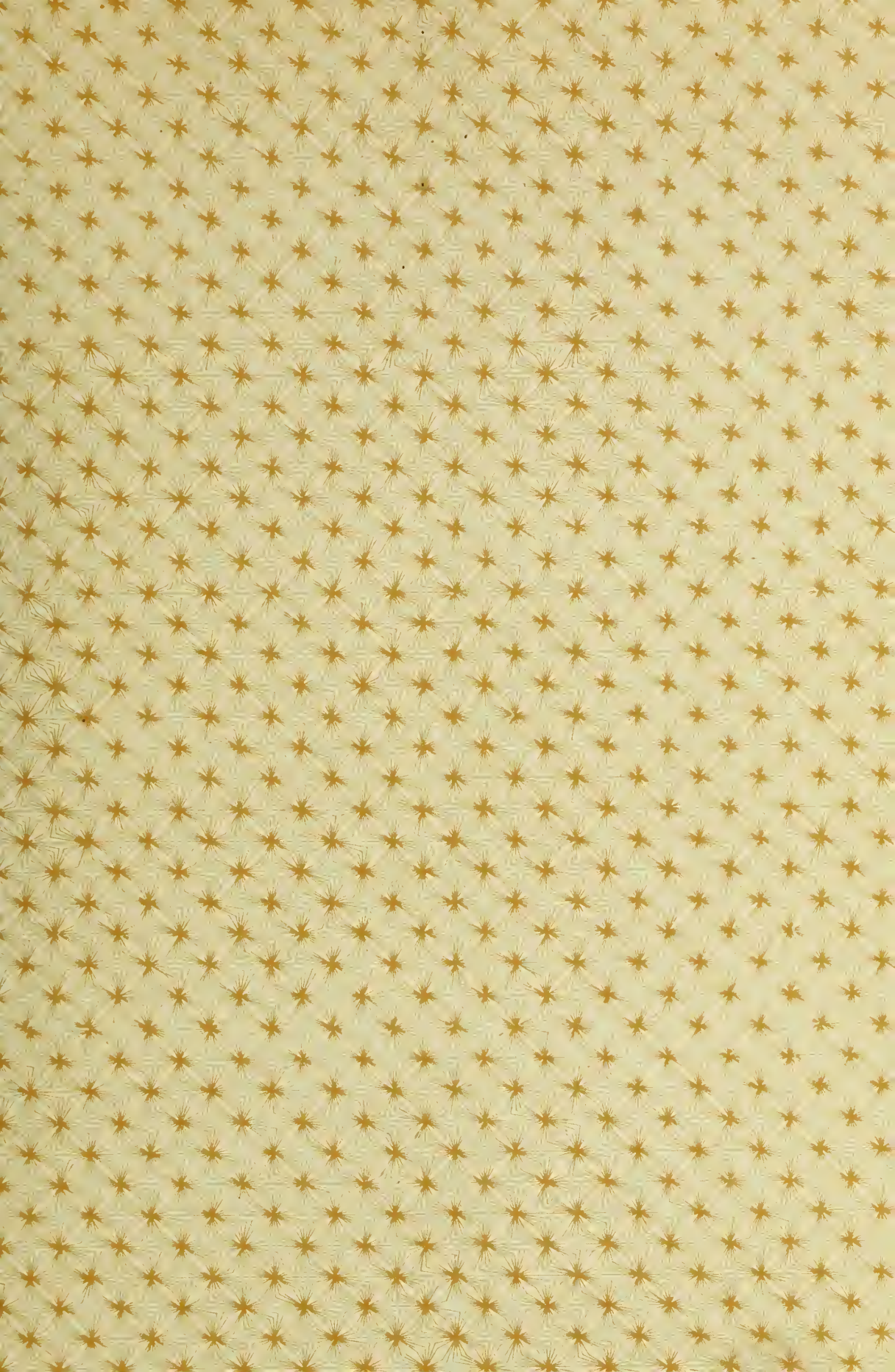
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A NEW GRAVIMETRIC METHOD FOR
THE DETERMINATION OF TITANIUM

BY

OSCAR S. WATKINS

THESIS

FOR

DEGREE OF BACHELOR OF SCIENCE

IN

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June 1[#] 1906.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Oscar S. Watkins,

ENTITLED A New Gravimetric Method For

The Determination of Titanium.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science.



HEAD OF DEPARTMENT OF Chemistry.

- The work of this thesis was done under the immediate direction
of Dr. James H. Walton, Jr.

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A NEW GRAVIMETRIC METHOD FOR THE DETERMINATION OF TITANIUM.

INTRODUCTION.

The methods for the gravimetric determination of Titanium which are used at the present time are those which have been used for the last twenty years or more, no recent method showing any improvement over the so-called standard methods. These methods are very long, and while they are capable of giving accurate results, they are entirely unsuited for analytical work in which a fair amount of rapidity is required. Many methods have been published which appear to possess advantages over the older methods, but they have not proven satisfactory. It is but recently that titanium has been of sufficient ~~technical~~ technical importance to demand better and more rapid methods for its determination.

It seems that no one experimenter has made a special study of the gravimetric methods of determination, but many have contributed methods. Among the methods which are used most frequently, and which appear in our best works on Quantitative Analysis are:



1. Gooch Method.¹
2. Baskerville's Method as revised by Sidener.⁴
3. Classen Method.⁵
4. Sodium Carbonate and double Potassium acid-sulphate Method.⁸
5. Weller Colormetric Method.⁹

The Gooch method is summarized as follows:-

Fuse the ore with sodium carbonate, leach with water, fuse the residue with potassium disulphate, dissolve melt in water, treat with tartaric acid, pass in hydrogen sulphide, filter off the iron sulphide, treat filtrate with potassium permanganate, sulphurous acid, neutralize with ammonium hydroxide, add acetic acid, boil the precipitate, collect on a filter, ignite and weigh. The method¹ in detail is as follows:-

Weigh out on a tared watch glass, 5 grams of the finely ground ore and fuse in a platinum crucible with 12 grams of sodium carbonate until it comes to a quiet fusion. This removes nearly all of the aluminum, ~~silica~~ and phosphorous, the titanium being left as the insoluble sodium titanate with the ferric oxide. Digest the melt on the steam bath until it separates from the crucible. Filter the residue on a small filter, wash with 2% sodium carbonate solution. Place filter paper and contents in a platinum crucible and ignite over a low Bunsen flame. When the filter paper is completely burned, heat in a flame of blast lamp for 5 minutes, then fuse with 8 grams of potassium acid sulphate for 1/2 hour, keeping the mass in a liquid state, and so that fumes of sulphuric anhydride evolve when the cover of the

crucible is raised. If the sulphate is added in successive small quantities, the danger of the fused mass boiling over is considerably lessened. Allow the melt to cool, then dissolve in 200 c.c. of cold water. The titanate acid, iron and other bases go into solution as sulphates, while any silica present remains as a residue. Saturate the hot solution with hydrogen sulphide and make slightly ammoniacal. By this means all of the iron is precipitated as ferrous sulphide, while the aluminum and titanium remain in solution. Filter off the ferrous sulphide and acidify the filtrate with sulphuric acid, heat to boiling and filter off the precipitate of sulphur and platinum sulphide (the latter from the crucible). Boil the filtrate to expel the last traces of hydrogen sulphide, and destroy the tartaric acid by adding 4 grams of potassium permanganate. Then add sulphurous acid until the precipitated manganese dioxide redissolves after which add a slight excess of ammonia, then 7 - 10 c.c. of glacial acetic acid for each 100 c.c. of the solution. Boil the solution one minute and allow the precipitate to settle and decant the filtrate through an ashless filter paper, transfer the precipitate to the filter, wash with 7% acetic acid and finally with hot water. Ignite the precipitate and filter paper in a weighed platinum crucible for 20 minutes.

The precipitate may contain manganese and alumina, and in order to eliminate them, fuse it with 3 grams of sodium carbonate for 30 minutes, leach the melt with cold water leaving the sodium meta-titanate and some alumina undissolved. Filter off the precipitate and ignite it in a platinum crucible, fuse again with 1/2 gram of sodium carbonate. After cooling, dissolve the

contents of the crucible in 2 c.c. of sulphuric acid (1 c.c. H_2SO_4 to 1 c.c. H_2O), dilute to 200 c.c. and treat with 5 grams of sodium acetate and 1/10 of its volume of glacial acetic acid. Boil one minute, allow the precipitate to settle, filter and wash the residue with 7% acetic acid, and finally with hot water, dry, ignite and weigh. The precipitate may still contain alumina, so fuse it again with sodium carbonate and treat the melt with sulphuric acid etc., as described above. Repeat the process until a constant weight is obtained.

Baskerville's Method⁴ as revised by Sidener seems to be an improvement over the other methods and is as follows:-

Fuse the ore with potassium acid sulphate and sodium fluoride. Then add sulphuric acid, dilute the mixture, treat with sulphurous acid, sodium acetate and acetic acid. Boil the mixture, filter off the precipitate, dry, ignite, and weigh. The method in detail is as follows:- Intimately mix one gram of the finely ground ore with 12 grams of potassium acid sulphate and 2 grams of sodium fluoride and fuse in a platinum crucible at a low heat until the mass is in liquid state, then keep the heat so regulated that the mass is just liquid, and that fumes of sulphuric anhydride evolve when the cover of the crucible is raised, until all the particles of the ore disappear. When the fusion is cool, add 3 c.c. of con. sulphuric acid and carefully heat the mass until it is just liquid. When the melt is cool, place the crucible with contents in a No. 5 beaker containing 200 c.c. of a 5% sulphuric acid solution. Heat so that the temperature of the beaker and contents does not reach a point which the palm of the hand cannot comfortably stand. The melt should dissolve completely to

a clear solution. The determination of the titanium dioxide is very similar to that method used by Gooch and is as follows:-

Add 50 ~~cc~~ c.c. of sulphurous acid to the clear solution and heat gently for 10 minutes. Cool the solution and neutralize with ammonia until the precipitate which forms just dissolves. Add 10 c.c. of sulphurous acid, 20 grams of sodium acetate and $\frac{1}{6}$ the volume of acetic acid(sp.gr. 1.04), and heat to boiling, when the titanium should separate out as a white flocculent precipitate. Digest on the steam bath for 30 minutes which insures complete precipitation of titanic acid. Allow the precipitate to settle, filter on an ashless filter paper, wash with 5% acetic acid, and finally with hot water. This precipitate is contaminated with iron, alkali sulphates, alumina, and phosphoric acid, and in order to eliminate these, ignite filter paper and contents in a platinum crucible until the carbon of the filter paper is burned, then fuse with 8 grams of sodium carbonate free from potassium carbonate, and 2 grams of sodium nitrate. This forms soluble phosphates and aluminates of sodium and at the same time converts the titanium into insoluble sodium titanate, and the iron into insoluble ferric oxide. An hour's fusion with the strong flame of the blast lamp is necessary to bring about these changes completely. Allow the melt to cool, then boil with a strong solution of sodium carbonate for 20 minutes, filter hot and wash with 10% solution of sodium carbonate. Collect the insoluble sodium titanate and ferric oxide on a filter paper and dry for one hour in an air bath at 110° C. Transfer the residue to a platinum crucible and burn the filter paper on a platinum wire and add the

residue to the crucible. Fuse the contents of the crucible with 2 grams of sodium carbonate and treat the cooled mass with 2 c.c. of sulphuric acid, 1 c.c. acid to 1 c.c. water and gradually apply heat until fumes of sulphuric anhydride evolve. Allow to cool, dissolve the pasty mass in a mixture of 200 c.c. of water and 20~~X~~ c.c. of sulphurous acid. Neutralize with ammonia until the precipitated titanic acid dissolves with difficulty, add 5 grams of sodium acetate in solution and 25 c.c. of acetic acid (sp.gr. 1.04). Boil for 1/4 hour, digest on a steam bath for 1/2 hour, filter the precipitate on an ashless filter paper, wash with hot 5% acetic acid, and finally with hot water. Ignite in a weighed platinum crucible over a blast lamp, heat for at least 20 minutes and weigh as pure titanium dioxide.

Classen's method⁵ of separating iron and titanium and determining the latter depends upon the fact that in an alkaline solution of hydrogen peroxide, titanium is held in solution, while iron is precipitated as ferric hydroxide. The procedure is as follows:-

Dissolve 1 gram of the ore in 10~~X~~ c.c. of concentrated hydrochloric acid, and precipitate as usual with ammonium hydroxide. Dissolve the precipitate of ferric hydroxide and titanic acid in hydrochloric acid (sp.gr. 1.12), add 50 c.c. of hydrogen peroxide, 25 c.c. of potassium hydroxide (sp.gr. 1.50), dilute to 500 - 1000 c.c., according to the amount of the precipitate and then allow the ferric hydroxide to settle. The titanium remains in solution. Pour into a beaker, allow to settle, and then siphon off an aliquot part. Wash the precipitate with a mix-

ture of hydrogen peroxide and potassium hydroxide in water (about 10% of potassium hydroxide) and continue the washing until a few c.c. of the filtrate give no test for titanium. Heat the alkaline filtrate containing the titanium in a covered dish on a water bath, to destroy the excess of hydrogen peroxide. Any yellow precipitate which settles out at this point, consists of titanium trioxide mixed with titanous acid. When the evolution of gas has ceased acidify the solution with hydrochloric acid, heat until the solution is colorless and add ammonium hydroxide in excess. Filter out the precipitated titanous acid, wash with hot water, ignite, weigh. Purify until constant.

The sodium carbonate and double fusion with potassium acid sulphate method⁸ is quite similar to the Gooch method¹. Fuse the finely ground ore with sodium carbonate, dissolve in hot water, filter, ignite residue, fuse in platinum crucible with potassium acid sulphate, leach with a weak solution of sulphurous acid, treat with acetic acid, sodium acetate and then boil. Collect precipitate on filter, ignite and weigh.

The method in detail is as follows:- Fuse 5 grams of the finely ground ore with 10 grams of sodium carbonate in the flame of a blast lamp until it comes to a quiet fusion. Cool and leach with hot water until the melt separates completely from the crucible. Filter on an ashless filter paper and wash with hot 2% sodium carbonate solution. Ignite the residue in a platinum crucible and fuse with 8 grams of potassium acid sulphate for 30 minutes. Cool and dissolve the melt in 400 c.c. of sulphurous acid which keeps the iron reduced in the ferrous state. Add 20 grams

of sodium acetate and 100 c.c. of acetic acid (sp.gr. 1.04). Boil for 10 minutes, allow the precipitate to settle, filter, wash with 5% acetic acid, ignite and weigh. This precipitate contains some iron and alumina as impurities, and in order to remove them, fuse again with 8 grams of potassium acid sulphate, and carry out exactly as before. The second weighing of the precipitate should correspond to the weight of the titanium dioxide in the sample.

Weller's Colormetric Method⁹ has given satisfactory results for ores containing less than 4% of titanium. It depends upon the fact that in acid solution titanium is oxidized to a higher oxide, probably titanium trioxide⁵ by means of hydrogen peroxide. This higher oxide colors the solution yellow to reddish, depending upon the amount of the titanium present and this gives a method for the colormetric estimation of the titanium. This method⁹ is the same as revised by Sidener⁴ up to the point of the solution of the potassium acid sulphate melt in cold water. Dilute the clear solution to 500 c.c. with 5% sulphuric acid and mix thoroughly. Put 50 c.c. into a comparison tube. Into a second comparison tube put as much of a standard ferrous ammonium sulphate solution containing 5% sulphuric acid as will contain an amount of iron equal to that in 0.1 gram of ore and dilute to 50 c.c. with 5% sulphuric acid. Add to each tube 5 c.c. of strong hydrogen peroxide and in addition, to the second a sufficient amount of a standard solution of titanium sulphate to match the color in the first tube. From the amount of the standard titanium solution required to give the color, calculate the percentage of titanium dioxide present in the sample.

The standard titanium sulphate solution may be prepared thus:- fuse 5 grams of pure titanium dioxide in a platinum crucible with 5 grams of potassium acid sulphate. Cool and dissolve the melt in 5% sulphuric acid. Dilute the solution with 5% sulphuric acid to 500 c.c.

The methods for determining titanium which have just been described have certain disadvantages. One which is characteristic of them all is that the amount of time required to carry through the determination is entirely too great.

Of the methods which have just been described the following were used for the determination of titanium in the ore which was used in this investigation. This ore was a titanium iron ore, and contained the usual impurities with the exception of phosphorous.

Gooch Method.

The main difficulty met with in the Gooch method in addition to length of time required for an analysis was in dissolving the precipitated manganese dioxide with sulphurous acid. This required a large volume of the latter, increasing the solution to such a volume that it was difficult to handle. By this method, only one determination of the ore was obtained. The amount of titanium dioxide present was found to be 10.54 percent.

Baskerville's Method.

Baskerville's method¹⁴ as revised by Sidener⁵ other than being a long determination possesses no disadvantages. The ore was found to contain 14.10% and 14.17% by this method.

Classen's and Weller's methods were not tried in

connection with this investigation.

The sodium carbonate and double potassium acid sulphate method⁸ ^{as} has _A its main difficulty the keeping of the iron reduced with sulphurous acid to prevent its separating out with the titanio acid. Four determinations were made of the ore by this method with the following percents of titanium oxide found to be present: 14.50, 14.11, 13.50 and 14.71.

Of the methods used in this investigation that of Baskerville as revised by Sidener seems to give the best satisfaction. The method other than being long ^{possesses} _A no difficulties characteristic of the other methods used, and in my estimation is preferable.

From the foregoing analyses, the mean of the results 14.10, 14.17, 14.11 was considered the true percent of the titanium in the ore, thus giving the value 14.13.

The object of this thesis was to find some method by which the ore could be decomposed, converting the titanium to a soluble form and at the same time separating it from the iron which causes the most difficulty in all determinations. The method⁵ used was suggested by Classen's method⁵, which depends upon the fact that in an alkaline solution of hydrogen peroxide, titanium is held in solution probably as titanium trioxide⁵ while any iron present is precipitated as ferric hydroxide. It was considered possible that the fusion of a titanium compound with sodium peroxide might give the same reaction as an aqueous solution of sodium hydroxide and hydrogen peroxide, that is, that by fusion the titanium would be oxidized to a compound corresponding to titanium

trioxide by the sodium peroxide so that on leaching the fused mass with water the titanium would dissolve in the alkaline solution, leaving the iron precipitated as ferric hydroxide. This fusion with sodium peroxide was tried qualitatively with pure titanium dioxide and also with a titanium iron ore. The results showed in each case that titanium is taken into solution, the iron in the case of the ore being left as the insoluble hydroxide.

EXPERIMENTAL.

(a) In order to learn whether other "per" salts react with titanium in a similar manner to sodium peroxide, a series of experiments was carried out, with the hope of decomposing the ore by means of another reagent, the violence of the reaction of sodium peroxide restricting its use to silver, nickel and iron crucibles.

The following experiments were carried out for this purpose, an iron crucible being used in each case.

(1). 0.5 grams of ore fused with 5 grams of $K_2C_2O_6$. Fusion clear, no titanium went into solution on adding water.

(2). 0.5 grams of the ore fused with 5 grams of $K_2S_2O_8$. Fusion not clear, did not dissolve but adhered to crucible.

(3). 0.5 grams of the ore fused with 5 grams $K_2C_2O_6$ and 5 grams $K_2S_2O_8$. Fusion not clear, no titanium went into solution.

(4). 0.5 grams of the ore fused with 7 grams $K_2C_2O_6$ and 3 grams $K_2S_2O_8$. Did not come to a clear fusion.

From this series of experiments it was concluded that under these conditions the other "per" salts do not react like the sodium peroxide, so they cannot be used to decompose the ore.

(b) Length of time of fusion.

(5) 1. gram of the ore fused with 10 grams of sodium peroxide for 10 minutes, test for titanium was given by the solution but fusion adhered to crucible.

(6). 1. gram of the ore fused with 10 grams of sodium peroxide for 20 minutes, fusion clear, titanium test given but fused mass adhered to crucible.

From this series of experiments it was learned that a fusion of 20 minutes gave better results than the shorter fusion. With sodium peroxide alone it was learned that satisfactory fusions cannot be obtained. It was found that if sodium carbonate is mixed with sodium peroxide, a satisfactory fusion results.

(c). Experiments to find the best proportions of mixture of sodium peroxide and sodium carbonate for this particular ore.

(7). 1. gram of the ore, heated with 6 grams of sodium peroxide and 4 grams of sodium carbonate for 20 minutes, would not fuse.

(8). 1. gram of the ore, heated with 6 grams of sodium peroxide and 2 grams of sodium carbonate for 20 minutes came to a molten condition, but adhered to crucible when water was added.

(9). 1. gram of the ore fused with 9 grams sodium peroxide and 2 grams sodium carbonate came to a clear fusion in 5

minutes but also adhered to the crucible.

(10). 1. gram of the ore fused with 10 grams of sodium peroxide and 1. gram of sodium carbonate came to a clear fusion in 5 minutes, vigorous action when treated with water, but also adhered to the crucible.

(11). 1. gram of the ore fused with 12 grams sodium peroxide and 1. gram sodium carbonate for 20 minutes. Fusion clear, vigorous action when water was added, dissolved completely out of crucible, gave test for titanium.

Thus it was found that sodium carbonate was necessary to aid the sodium peroxide to decompose the ore, and that the proportions for this particular ore are 12 grams of sodium peroxide to 1 gram of sodium carbonate.

(d). Influence of the temperature at which the fusion is made.

(12). 1. gram of the ore fused with 12 grams of sodium peroxide and 1 gram sodium carbonate for 20 minutes, treated with water, tested for titanium, showed it to be present. The heat was from a low flame of a Bunsen lamp.

(13). Same experiment except the fusion was for 25 minutes at a high heat. Dissolved out completely but gave no test for titanium.

Thus it was found that in order to decompose this ore and keep the titanium in solution the fusion must be carried on at a low temperature.

(e). Experiment to find method of dissolving fusion.

(14). 1. gram of the ore fused for 20 minutes in an iron crucible at a low heat. The crucible and contents were allowed to cool, then placed in a 400 c.c. casserole, and a stream of water from a wash bottle directed on the fused mass. Vigorous action took place and the mixture became hot. Allowed action to cease, diluted contents of casserole to 500 c.c. in a graduated flask. Allowed the precipitated ferric hydroxide to settle, then 200 c.c. of the clear solution was filtered off into a clean beaker. This filtrate on being tested showed no iron to be present. The titanium was determined by boiling in the usual way with sodium acetate and acetic acid. 9 percent of titanium dioxide was found to be present. The precipitate was not purified.

(15). 1. gram of the ore was similarly treated, but was allowed to go into solution, cooled by immersing crucible and contents in a beaker of 400 c.c. of cold water. The titanium dioxide was determined, 13.40 percent of the unpurified titanium dioxide being found.

Thus in order to get a complete solution of the titanium, it must be dissolved out of the mass cold, since the heat generated when the fusion is dissolved in a small amount of water seems to break up the soluble titanium compound.

(f). Experiment with a larger amount of ore.

(16). 1.5 grams of the ore was fused with 12 grams of sodium peroxide and 1 gram of sodium carbonate in an iron crucible for 20 minutes using a low flame. The mass was allowed to cool, then was immersed in a beaker containing 600 c.c. of cold water. When the vigorous action had ceased, removed the crucible, washed

it thoroughly, and transferred the solution to a litre graduated flask and diluted to mark. Filtered off a portion of the clear solution, discarded the first 25 c.c. and took 500 c.c. of the filtrate. This was acidified with sulphuric acid, 20 grams of sodium acetate and 90 c.c. of acetic acid (sp.gr. 1.04) were added and boiled until the titanous acid separated out. This required one and one-half hours boiling, as it was necessary to expel the excess of hydrogen peroxide before the titanium would precipitate. This excessive boiling was avoided hereafter by destroying the hydrogen peroxide with 50 c.c. of sulphurous acid. The precipitate was allowed to settle, filtered on an ashless filter paper, ignited and weighed. This determination gave 17.97 percent of titanium present in the ore.

(g). Purification of the precipitate.

(17). In order to show whether or not the precipitate contained silica as an impurity, 2 c.c. of con. sulphuric acid, 1 c.c. of water and 4 c.c. of hydrofluoric acid were added to the platinum crucible. On evaporating to dryness, igniting and weighing the precipitate there was no loss in weight, showing that the silica had been previously removed. The principle impurity, therefore, is alumina. In order to remove it the following method of purification was tried.

(18.) The precipitate was fused with 10 grams of sodium carbonate for 20 minutes. The melt was boiled with 25% sodium carbonate solution and filtered. The residue was washed with 2% sodium carbonate solution, then dissolved in 10 c.c. of hot con. hydrochloric acid. The dissolved residue was neutralized with

sodium carbonate, then treated with 20 grams of sodium acetate and 50 c.c. of acetic acid. This mixture was poured into a beaker containing 400 c.c. of boiling water, the precipitate of titanitic acid was formed at once, was allowed to settle, filtered, ignited and weighed. During this purification over 4% was lost. Several determinations were made by this method with the following results; 16.75%, 17.97% and 15.94% before purification and 12.60%, 14.84% and 12.91% respectively after purification. It was thought probable that this disagreement might arise from the method of purification. To test this method, .12 grams of pure titanium dioxide was fused with 7 grams of sodium carbonate and purified as above with the following results: weight of pure titanium dioxide taken, two samples of .12 grams each, weight found after purification .0677 and .0683 grams. The above method of purification, therefore, is very inaccurate.

Gooch's method of purification as given by Treadwell² was then tried, and a series of experiments run in order to test the accuracy of the sodium peroxide method, with the following results: percent of titanium peroxide 13.56; 13.33; 13.10; 13.45; 13.45; with the mean of 13.38.

CONCLUSION.

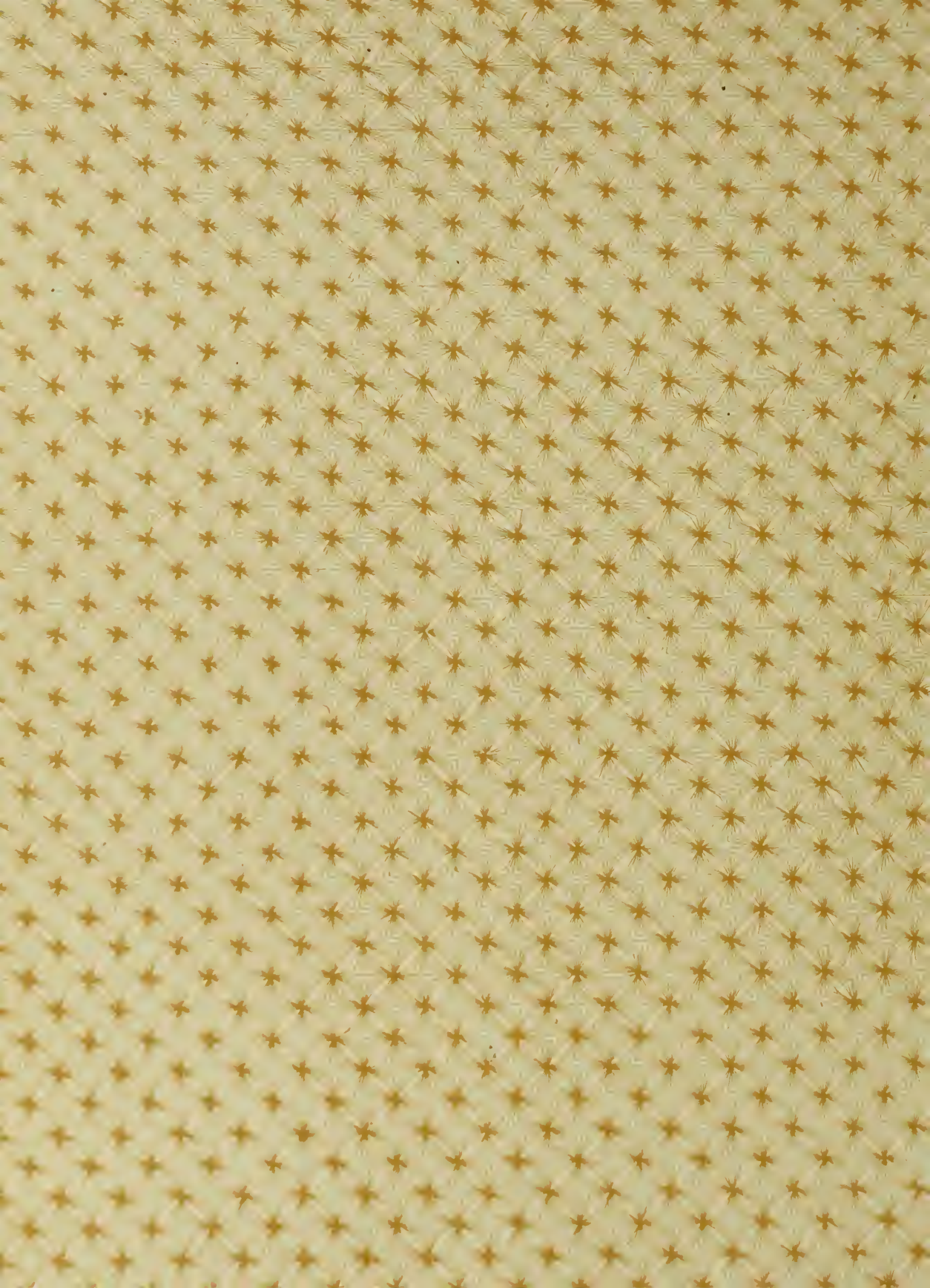
The values for the amount of titanium in the ore obtained by the method worked out in this investigation will be

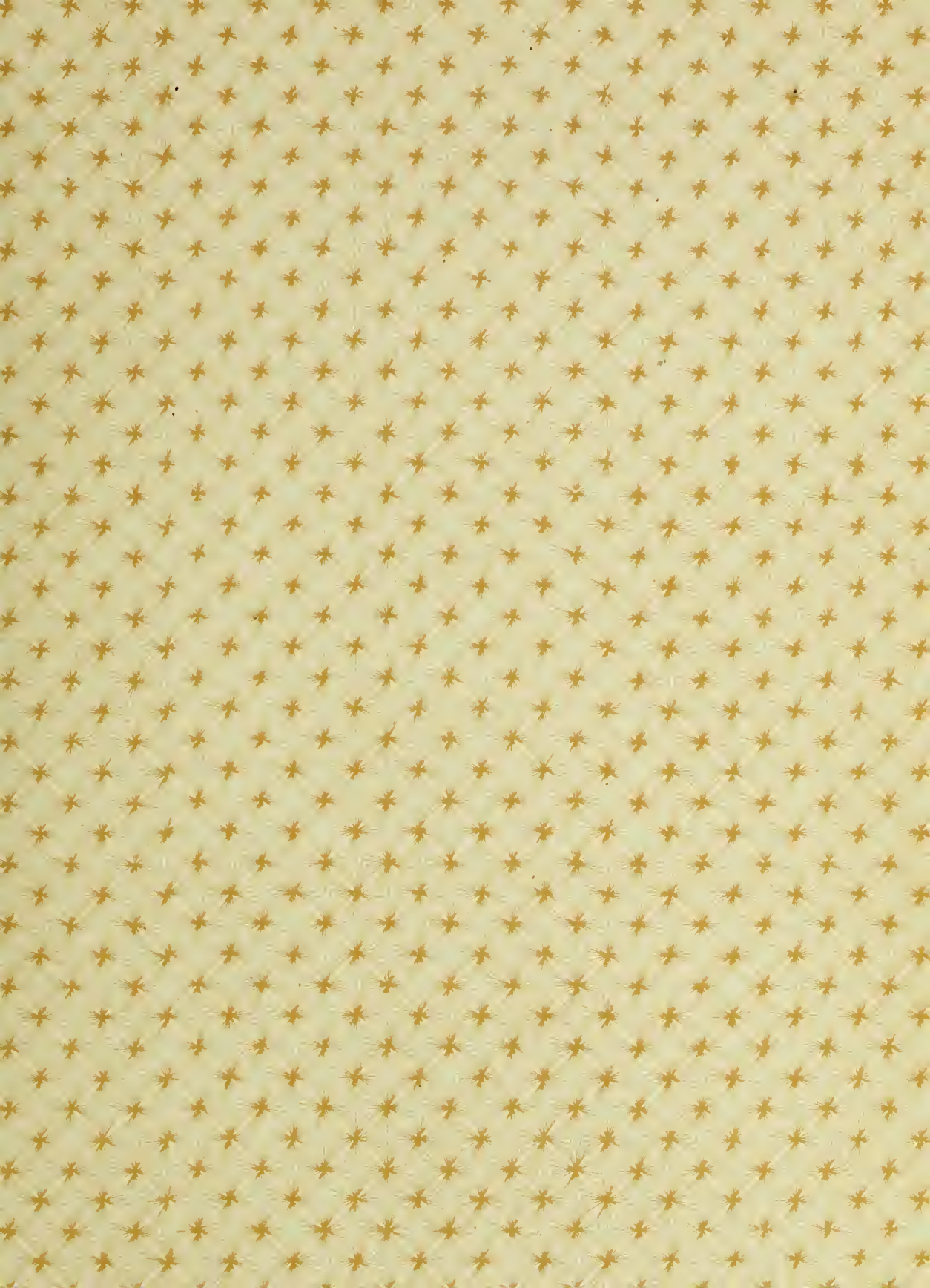
seen to agree with each other, but their mean (13.38) is considerably lower than the value (14.13) obtained for the ore by the standard methods in use at the present time. The source of the error which causes the difference may lie in one of three parts of the determination; decomposition, precipitation or solution. That it is not due to incomplete decomposition is evident from the fact that the ferric hydroxide left after dissolving sodium peroxide fusion in water is completely soluble in acid and shows no particles of undecomposed ore.

The precipitation as carried out is made under exactly the same conditions as in the determination of titanium by standard methods-: consequently it should be as complete as when those methods are used. That this is true is borne out by the fact that the filtrate from the titanium precipitation on being tested with hydrogen peroxide and sulphuric acid gave no test for titanium. It seems logical, therefore, to conclude that the source of error must lie in incomplete solution, a certain amount of the titanium remaining with the ferric hydroxide. Further experiments to eliminate the error should be directed toward this part of the determination.

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